

A PHYSICAL AND CHEMICAL BASIS FOR UNDERSTANDING INORGANIC MINERAL TRANSFORMATIONS IN COALS BASED ON MODEL-MINERAL EXPERIMENTS

S. Srinivasachar, J.J. Helble, and A.A. Boni
PSI Technology Company
Research Park, P.O.Box 3100
Andover, MA 01810

Abstract

Ash deposition depends on the size, surface composition and surface state of the transformed coal minerals. It is currently assumed that the minerals found in coals can be described in terms of their elemental chemical oxides. We hypothesize that each mineral represents a unique physico-chemical entity that undergoes a complex transformation as it is processed by the combustion environment and eventually reaches an oxidized state. We have performed drop-tube furnace experiments, with representative combustion conditions, on two important coal minerals: pyrite and illite. Comparison is made with an Eastern coal containing large quantities of the above minerals. There is evidence of exothermic and endothermic reactions, fragmentation, kinetic and transport-limited oxidation, and formation of both complex glasses and crystalline phases, at different stages in the mineral transformation process. These processes determine the final size, composition, and the surface state of the ash, which cannot be predicted by thermochemical methods alone.

INTRODUCTION

Ash deposition on heat transfer surfaces is the most severe problem associated with the combustion of coal. Besides lowering heat transfer rates, hence plant efficiencies, frequent maintenance and unscheduled shutdowns for removing these deposits substantially adds to the cost of power generation. It is therefore critical that for a given pulverized coal (p.c.) fired boiler, appropriate coals be selected and operating conditions be maintained to minimize ash deposition and its detrimental effects. Presently, empirical indices based on the elemental oxide composition are used to rank a coal's fireside behavior.^{1,2} These slagging and fouling "factors" are only applicable to very specific types of coal, coal ash and boiler units and extension of these factors to different coal/ash types or combustion conditions gives results which are uncertain at best. This can be attributed to the fact that different coals contain different amounts and species of minerals,³ and their specific physical and chemical transformations govern the state in which they arrive at a heat transfer surface and deposit. Slagging and fouling factors that are defined and used at present average out the expected behavior of the coal ash, i.e. they consider the coal and ash to be homogeneous and represented as a sum of individual elemental oxides. The detrimental deposition characteristics of ash resulting from some problematic individual minerals or their combinations is thus masked out. An understanding of the transformations of individual minerals in coal is therefore needed to develop a better predictor for ash deposition.

Iron and alkali-bearing minerals, for example, pyrite and illite respectively have long been recognized as a major source of wall slagging. The behavior of excluded pyrite particles under combustion conditions has been

reported by our group in detail previously^{4,5} and is only summarized here. The focus of this article is on transformations of illite under similar processing conditions. The stickiness characteristics of illite transformed in a combustion environment is also examined.

EXPERIMENTAL

All combustion and deposition experiments were performed in a resistance-heated entrained flow reactor, operated under laminar flow conditions. Schematics and detailed description of the reactor is given elsewhere⁶ and the deposit collection probe is shown in Figure 1. Samples of size-graded illite were entrained in an air stream and injected axially into the isothermal furnace via a water-cooled injector at a rate of about 0.3 gm/minute. Air was used as the furnace gas, and was injected separately through the top of the reactor. Gas temperature was held at 1500 K for the transformation experiments, but was varied for the stickiness determination experiments. For the former set of experiments, the particle residence time was varied from 0.8 to 2.5 seconds in the isothermal section, while it was held constant at 2.5 seconds for the stickiness tests.

The particles were collected via one of the following techniques:

1. isokinetic sampling, via a water-cooled, nitrogen-quenched probe. At the exit of the probe, all particles passed through a seven stage Pollution Systems Control Corp. cascade impactor, providing on-line size classification of all particles larger than 0.1 microns. Smaller particles were collected on a backup filter. In experiments where size classification was not required, a total filter was used.
2. deposition of a portion of the supermicron particles on a deposit collection probe. The capture efficiency is determined from the ratio of the mass of the deposit on the mullite tube to the mass of the particles that passed through the projected area of the substrate tubes. The gas temperatures at the deposition location, although intended to be the same as the furnace temperature, are 70 - 100 K lower.

Chemical Analysis of Illite

The illite examined in this study was a Cambrian shale from the Silver Hill formation, Jefferson Canyon, Montana. This illite has been characterized in detail by Hower et al.. The chemical composition (weight percent) of Silver Hill illite is as follows: SiO₂ (55.1), Al₂O₃ (22.0), K₂O (8.0), FeO (1.34),

Fe₂O₃ (5.3), MgO (2.8), Na₂O (0.08), H₂O- (1.0), H₂O+ (6.4). H₂O- represents the

weight loss at 110°C while H₂O+ is the weight loss on ignition. The composition of illite in various coals may be slightly different from each other, and therefore their behavior in the furnace may be somewhat different. One of the anticipated differences could be the fraction of the iron that is present in the ferrous state, as this will have significant impact on the its melting characteristics. However a study of Silver Hill illite can provide information as to the transformations undergone by "generic" illite in the combustion zone.

RESULTS AND DISCUSSION

Transformations of Illite

Samples of illite in the size range of 53 to 75 microns, exposed to high temperatures in the reactor for different residence times were examined by scanning electron microscopy (Figure 2). Illite particles in the feed are angular with an aspect ratio of about 1.5 to 2.0 for most particles. Upon exposure to 1500 K for a residence time of approximately 0.9 seconds, the color of the sample changed from a greenish gray to dark brown reflecting the oxidation of iron to the ferric state. Particles lose their angular form partially (Figure 2b) and vitrification is evident, although the overall morphology still resembles that of the original particle. Also isolated pore formation and gas evolution through these pores is evident. Examination of particles subjected to 1500 K for 2.5 seconds, shows that a much larger fraction had completely molten (Figure 2c). Several large pores are present on the particle surface, suggesting gas evolution and even some bloating as a result of trapped vapor trying to escape through a molten matrix. Gas evolution during heating consists of the release of the chemically bound hydroxyl groups. At slow heating rates, dehydroxylation does not occur until 600-700°C. At the high heating rates in our experiments, even higher particle temperatures would be reached before this step occurs. This endothermic step further delays the breakdown of the illite structure and its transformation into a glass.

The equilibrium behavior of illite can be determined from the $K_2O-Al_2O_3-SiO_2$ phase diagram. The phase diagram (Figure 3) shows that the minimum melting point appropriate to illite composition is 985°C. With addition of MgO and other components (particularly FeO, Fe_2O_3), a much lower eutectic melting point would be expected. The behavior of illite during the firing of ceramics was studied by Segnit and Anderson in an electric muffle furnace at heating rates of 100°C per hour and a soaking time of 4 hours. Clearly under these conditions one would be closer to equilibrium than in our experiments. They determined that glass formation started at 850°C, and vitrification was complete at 1000°C. Some pore formation was seen at 1050°C, and much more bloating and pore opening was evident at 1100°C. A comparison of the equilibrium behavior and the Segnit and Anderson work with our results shows that the transformations of illite under p.c. firing conditions would not approach the equilibrium condition, either during the heat-up stage or while cooling, for example when approaching a heat transfer surface after combustion has been completed. One would expect that under actual combustion temperatures which are higher than in our experiments (1500°C), and given that illite is associated with the coal during combustion (hence, even higher particle temperatures), illite will be completely molten before it arrives at a deposition surface. It then becomes important to describe the phase change kinetics and their impact on viscosity as the ash particle cools down. This transient viscosity variation will determine the deposition potential of the incoming ash particles.

Composition analysis of the raw and transformed illite particles was performed to determine if there was any preferential movement of potassium or iron to the particle surface. Surface analyses proved inconclusive since there was considerable compositional variation between different particles. A clearer picture of the selective mobilization of specific elements can only be obtained

by analyzing the particle cross-sections. We intend to do this as a next step. We also determined size distribution of the burnt illite particles using the cascade impactor. Data showed that all the particles were collected on the top stage of the impactor ($d_p > 8$ microns). This means that there is no vaporization of the illite (especially of the potassium) when it is not associated with carbon, nor any fragmentation into the 1 - 5 micron size range. Association with carbon would only mean that it would melt more quickly, thus impeding any fragmentation, although the higher temperatures might cause some vaporization.

Stickiness Behavior

Capture efficiencies of transformed illite particles were determined in the manner described in the experimental section. The capture efficiency is the fraction of the particles that both impact and stick. Impaction efficiency is determined from Stokes number considerations, and for the particle size (53-75 microns) and the velocity range used here, the impaction efficiency is unity. Figure 4 shows the capture efficiencies for different furnace temperatures and particle impaction velocities. When examined as a function of temperature, there is a dramatic increase in the rates of capture above 1400 K, except for the highest velocity. As the temperature is increased, the viscosity of the incoming particles decrease, and below a critical viscosity (approximately 10^7 poise) the particles are sufficiently deformable that the energy of impact is dissipated, and the particles stick without rebounding. One would normally expect that the capture efficiency would increase as the particle velocity increases - however, in our case the particles are large enough that all of them impact even at the lowest velocity. The observed reduction in the capture efficiency with increasing velocity must therefore be due to deposit erosion from the incoming particles. Microscopic observation of the deposit also showed that it was bonded at the higher temperatures, whereas at 1400 K, even though the capture efficiencies were high, the deposit was powdery and very friable. Quantitative analysis of these data will require consideration of both deposition and erosion.

Comparison of Illite and Pyrite Transformations

In a previous study,^{4,5} the transformations of pyrite were examined in the same entrained flow reactor setup. A comparison shows that the physical and chemical changes associated with the oxidation of pyrite is much more complex than for illite. Pyrite decomposed to pyrrhotite ($\text{Fe}_{0.877}\text{S}$), and this was followed by its oxidation to a molten sulfide-oxide mixture, subsequent crystallization of magnetite (Fe_3O_4) from the melt, and finally formation of hematite (Fe_2O_3). Particle temperature exceeds the gas temperature during this process due to the exothermic oxidation of sulfide. There was also a residence time region in which the particle remained molten. This constituted 80 percent of the total time for oxidation to magnetite. But, once magnetite formation was completed, the particle solidified, so that deposition was favored only as long as the pyrite was partially oxidized. Illite, on the other hand, does not exhibit such dramatic changes upon heating. Once the illite particle is molten, it is expected to remain as such until the gas, hence particle, temperature is lowered. Besides the formation of glass, the predominant reaction for illite seems to be the loss of the hydroxyl group, an endothermic reaction. Further analysis by EXAFS and Mossbauer techniques would reveal how the chemical

structure of iron and potassium in the illite-derived glass changes.

Based on limited data on the behavior of the minerals in coal,¹¹ the similarity with the behavior of the pure minerals is borne out. In Kentucky #11 coal, where the minerals are finely and uniformly dispersed through the coal matrix, examination of the ash size distribution showed that a large degree of coalescence was taking place. The final ash composition showed glasses with compositions ranging between illite, kaolinite, and silica, suggesting that the molten illite had incorporated the other minerals within its matrix. This data are also not inconsistent with little fragmentation seen with pure illite and that illite is expected to melt under combustion conditions. Mossbauer data on iron showed that only a small portion of the iron was in a glass, and the level of iron present as hematite increased as the oxygen level in the gas was raised.⁴ This is consistent with model calculations for oxidation of the pure mineral.

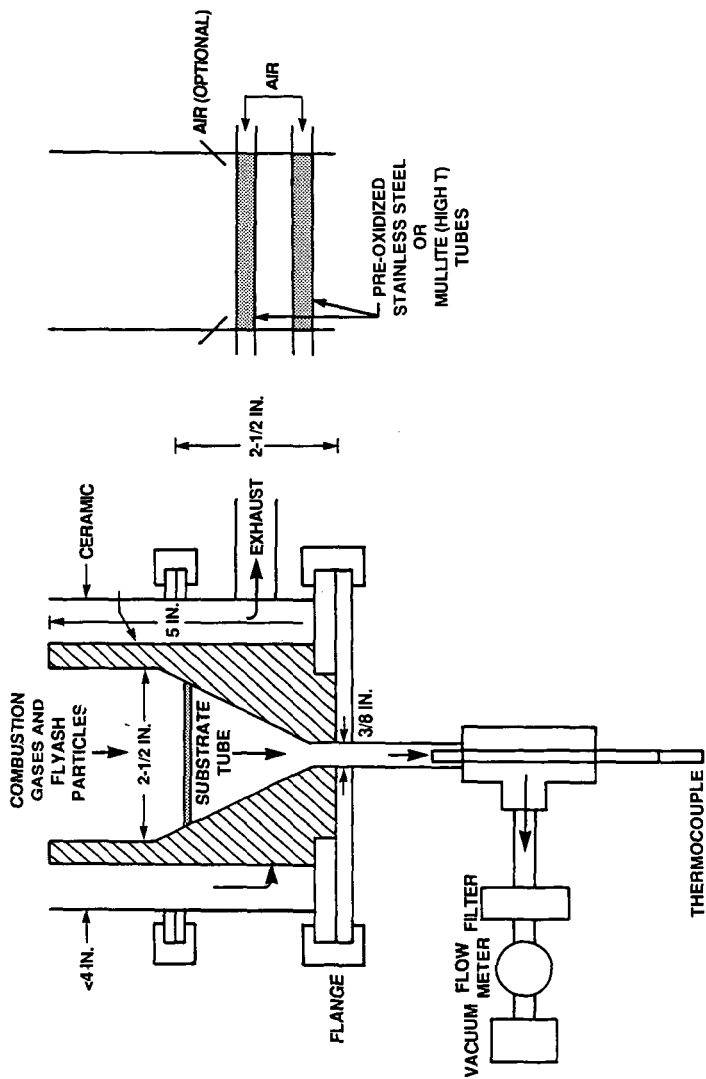
ACKNOWLEDGEMENTS

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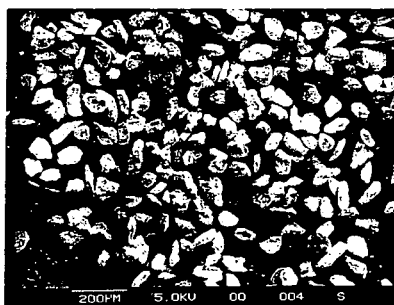
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STICKY PROBE

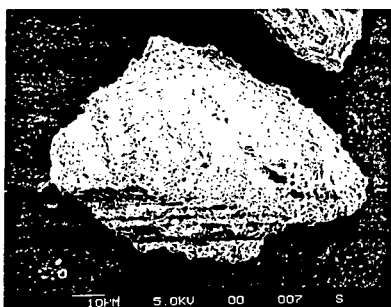


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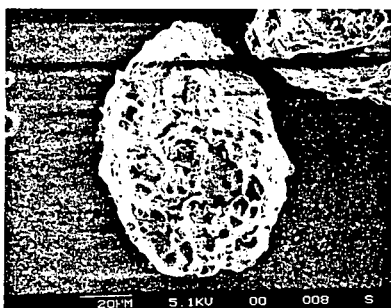
Figure 1. Schematic of the deposit collection probe



a)



b) Res. time ~0.9 seconds



c) Res. time ~2.5 seconds

Figure 2. Scanning Electron Micrographs of a) raw and b), c) Burnt Illite at Different Residence Times ($T_{\text{gas}} = 1500\text{K}$) for 53-75 Micron Particle Size Fraction

$K_2O-Al_2O_3-SiO_2$

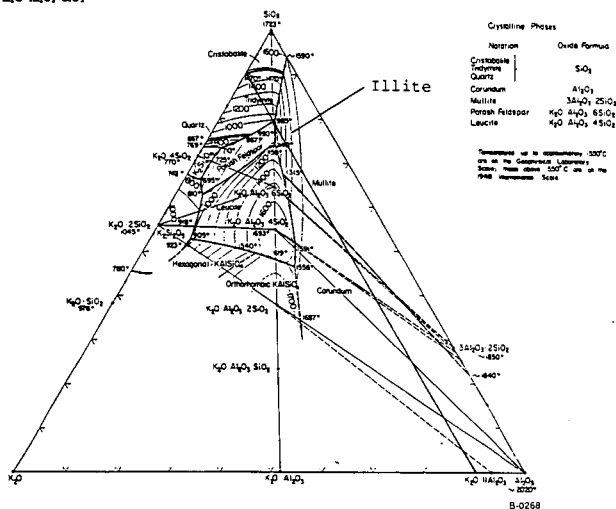


Figure 3. System $K_2O-Al_2O_3-SiO_2$; Composite. E.F. Osborn and Arnulf Muan, Revised and Redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 5, Published by the American Ceramic Society and the Edward Orton Jr., Ceramic Foundation, 1960.

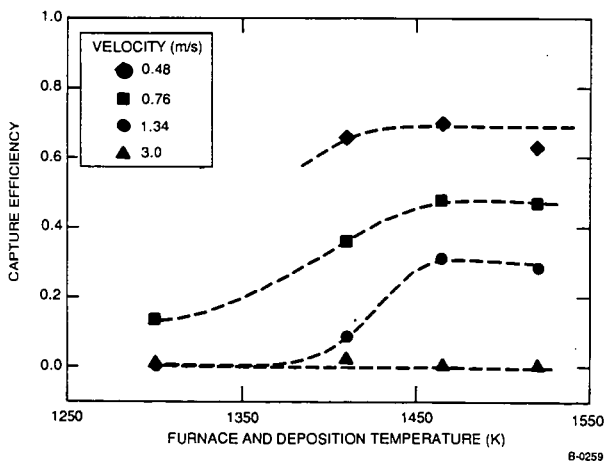


Figure 4. Capture Efficiencies (slagging probe) for Burnt Illite at Different Furnace Temperature and Particle Impaction Velocities